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14. ABSTRACT  Inorganic fillers are extensively used to modify polymer properties. Additionally, many nanoparticle fillers have been found to increase the thermal oxidative stability of modified plastics. Typically, good nano-dispersion is required to obtain significant property improvements. This is often achieved by compatibilizing the inorganic filler with the polymer host. The addition of organic groups to an inorganic particle leads to improved blending characteristics, while reactive groups increase their mechanical robustness if they are chemically incorporated into the host polymer. By modifying this organic functionality, nanoparticles can be fine-tuned to improve polymer hydrophobicity. For example, fluorinated nanoparticles can improve polymer hydrophobicity.					
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# SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED EIGHT-MEMBERED CYCLIC SILICATES

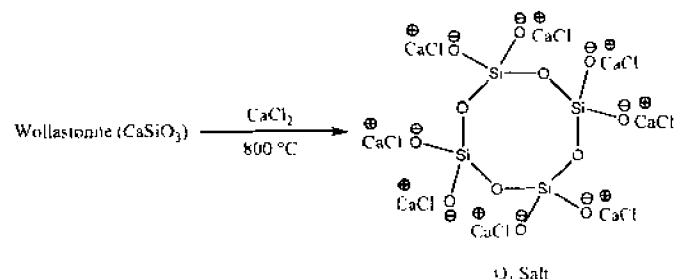
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## Introduction

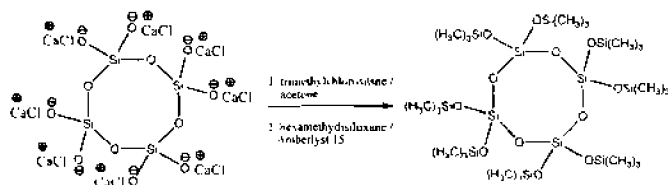
Inorganic fillers are extensively used to modify polymer properties. Additionally, many nanoparticle fillers have been found to increase the thermal oxidative stability of modified plastics. Typically, good nano-dispersion is required to obtain significant property improvements. This is often achieved by compatibilizing the inorganic filler with the polymer host. The addition of organic groups to an inorganic particle leads to improved blending characteristics, while reactive groups increase their mechanical robustness if they are chemically incorporated into the host polymer. By modifying this organic functionality, nanoparticles can be fine-tuned to improve desired polymer properties. For example, fluorinated nanoparticles can improve polymer hydrophobicity.

Polyfunctional eight-membered cyclic silicates are a class of inorganic nanoparticles that have the ability to be substituted with eight functional groups. The octakis[chloro calcium oxy]cyclotetrasilicate ( $Q_4$  salt) is produced from wollastonite, a naturally occurring mineral. When wollastonite is heated in the presence of calcium chloride (see Fig. 1),<sup>3</sup> the resulting  $Q_4$  salt is easily isolated. The silanolate functionality can then be derivatized using chlorosilanes. Upon substitution,  $Q_4$  compounds contain two types of silicon, M & Q. Silicon atoms bonded to one oxygen atom and three organic groups are in the M class. Silicon atoms bonded to four oxygen atoms are in the Q class. Substituted  $Q_4$  compounds contain eight M silicon atoms on the outer periphery and four Q silicon atoms in the ring.



**Figure 1.** The conversion of wollastonite ( $\text{CaSiO}_3$ ) to  $Q_4$  salt (octakis[chloro calcium oxy]cyclotetrasilicate).

Refinements of the functionalization of the  $Q_4$  salt have increased yields over reported values.<sup>3</sup> A greater variety of functional groups are now available for attachment to the core ring. The process in this report is two steps, but yields have increased from 30% to over 50% for non-fluorinated alkyl groups. The desired chlorosilane is first reacted with the  $Q_4$  salt, followed by the corresponding disiloxane in the presence of Amberlyst 15 ion-exchange resin<sup>4</sup>.



**Figure 2.** The substitution of  $Q_4$  salt.

## Experimental

**Materials.** Dimethylchlorosilane (Gelest) and vinyltrimethylchlorosilane (Gelest) were vacuum transferred before use. (Heptadecafluoro-

1,1,2,2-tetrahydrodecyldimethylchlorosilane (Gelest), 1,3-divinyltetramethyldisiloxane (Gelest), hexamethyldisiloxane (Gelest), wollastonite 520U (Fibertec), Amberlyst 15 ion-exchange resin (Aldrich), silica gel (Analtech), ACS grade acetone (Sigma-Aldrich), and reagent grade ethanol (Aldrich) were used as received.

**Instrumentation**  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR spectra were obtained on a Bruker AMX-300 spectrometer using 5 mm OD glass tubes. Sample concentrations were approx. 10% (w/v) in  $\text{CDCl}_3$  and were referenced internally to residual  $\text{CHCl}_3$  at 7.26 ppm ( $^1\text{H}$ ) and 77.0 ppm ( $^{13}\text{C}$ ). Contact angles were measured on a Dataphysics OCA 20 goniometer with a 3  $\mu\text{L}$  water drop size.

**Synthesis of octakis[chloro calcium oxy]cyclotetrasilicate ( $\text{Ca}_4(\text{SiO}_3)_4\text{Cl}_8$ ).** Wollastonite (19.8 g, 0.170 mol) and calcium chloride dihydrate (50.0 g, 0.340 mol) were ground together in a mortar and pestle, placed in a graphite boat, and heated in a tube furnace with a nitrogen purge at 800  $^\circ\text{C}$  for 24 hours. The mixture was allowed to cool to room temperature under nitrogen. The resulting white solid (58.4 g) was ground in a mortar and pestle. Ethanol (150 mL) was added to the mixture to extract excess calcium chloride. The solution stirred for 90 minutes, followed by a vacuum-assisted filtration to isolate the  $Q_4$  salt. The filtrand was dried in a vacuum oven at 74  $^\circ\text{C}$  for 85 minutes.

**Synthesis of octakis (trimethylsiloxy) cyclotetrasiloxane.**  $Q_4$  salt (10.2 g, 11.2 mmol) was placed in a 500 mL round bottom flask, acetone (300 mL) was added, followed by a condenser on top of the flask with a nitrogen purge. Trimethylchlorosilane (16.5 g, 152 mmol) was added through the top of the condenser. The solution was refluxed for 24 hours, cooled to room temperature, filtered to remove calcium chloride, and the filtrate volatiles were removed by vacuum. Hexamethyldisiloxane (40 mL) was added to the solid, along with Amberlyst 15 (1.0 g). The solution stirred for two hours at room temperature. The Amberlyst 15 was then removed by filtration and the excess hexamethyldisiloxane was removed by vacuum. The resulting solid was dissolved in hexane and two water extractions were performed to remove residual acid. The compound (5.06 g, 51% yield) was isolated and purified by sublimation.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm) 0.12 (s).  $^{13}\text{C}$  ( $^1\text{H}$ ) NMR ( $\text{CDCl}_3$ , ppm) 1.57 (s).  $^{29}\text{Si}$  ( $^1\text{H}$ ) NMR ( $\text{CDCl}_3$ , ppm) 9.8 (s), -108.3 (s).

## Results and Discussion

Substituted cyclic silicates with  $-\text{Si}(\text{C}_6\text{H}_5)_2\text{R}$ , where  $\text{R} = \text{CH}_3$ , vinyl, or  $(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3$ , have been prepared with many yields exceeding 50%. Yields of fluorinated compounds have not increased over previously reported values.<sup>5</sup> The  $Q_4$  salt is first reacted with chlorosilane, which replaces the majority of the  $\text{CaCl}$  groups on the  $Q_4$  ring. The partially substituted  $Q_4$  ring is then reacted with the corresponding disiloxane and Amberlyst 15 ion-exchange resin. The ring is fully substituted after two hours of stirring.

Fluorinated  $Q_4$  compounds, chemically similar to fluorinated POSS, have the potential to increase hydrophobicity in polymer nanocomposites.  $Q_4$ fluorodecyl<sub>8</sub> has been used to increase the water contact angles on various substrates, which were dipped into a  $Q_4$ -solution and then dried. The control solution contained AK225 and Tecnoflon (5 mg/mL), which was compared to a solution containing AK225, Tecnoflon (5 mg/mL), and  $Q_4$ fluorodecyl<sub>8</sub> (5 mg/mL). The increase in water contact angle was 23 degrees for the glass substrate and 16 degrees for the aluminum foil substrate. Oleophobicity has not yet been tested.

## Conclusion

An improved technique has been used to increase the yields of various substituted  $Q_4$  compounds, which have been characterized by NMR. The fluorinated version has been observed to increase water contact angles by over 15 $^\circ$  on various substrates.

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